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AMENDED SPECIFICATION

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PATENT SPECIFICATION

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NO DRAWINGS

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COMPLETE SPECIFICATION

Polyarylsulphone Polymers

We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation of the State of Delaware, United States of America, of 2501 Hudson Road, Maplewood, Saint Paul 19, Minnesota, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to thermoplastic polymers and to processes for preparing same.

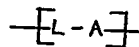
The polymers of the invention are high molecular weight condensation polymers comprising polyaryloxysulphones which are characterised by a high degree of thermal and chemical stability.

Polyphenylsulphones have been reported heretofore, as by Weil, Compt. Rend. 254, 3674 (1962), and as described by Kreuchunas in U.S. Patent No. 2,822,351. However, these have been either insoluble or low molecular weight materials which were not suitable for the production of shaped articles; or they have been susceptible to chemical oxidation, thus reducing their utility. Moreover, the heretofore available processes have failed to permit the preparation of polymers of this type which form films or filaments of good physical properties.

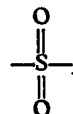
It has now been found that soluble, high molecular weight polyaryloxysulphones can be produced from aromatic disulphonylchlorides by condensation with aromatic hydrocarbons,

or by self condensation of certain aromatic monosulphonyl chlorides.

According to the invention there is provided a thermoplastic substantially linear soluble polymer which is capable of forming self-supporting films, and which consists of repeating units of the formula:

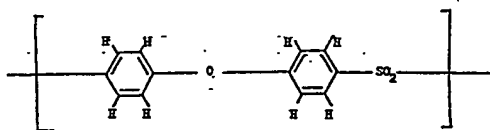


in which A represents an aromatic group, and in from 10 to 50 percent of the units, L represents the simple linkage ---O--- , and in the other units, L represents the linkage

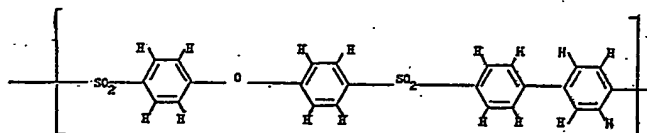


each aromatic group represented by A being connected to no more than one linkage L represented by the simple linkage ---O--- , the polymer having an inherent viscosity (as herein defined) of not less than 0.3, with the exception of the following polymers a to e when prepared by melt condensation:

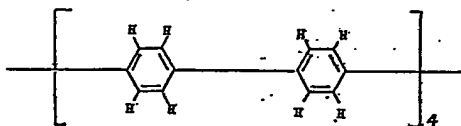
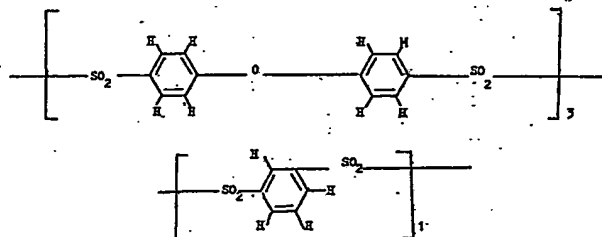
a) polymers consisting of repeating units being the formula:



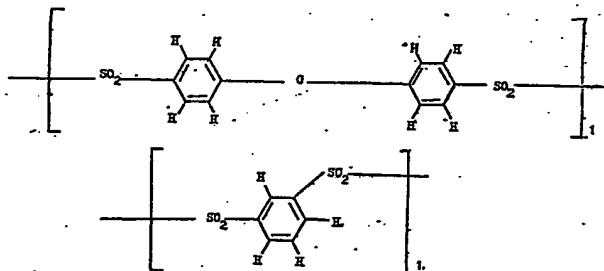
b) polymers consisting of repeating units of the formula:



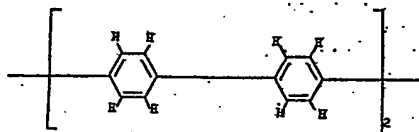
5 c) polymers consisting of repeating units of the following formulae in the numerical proportions shown:



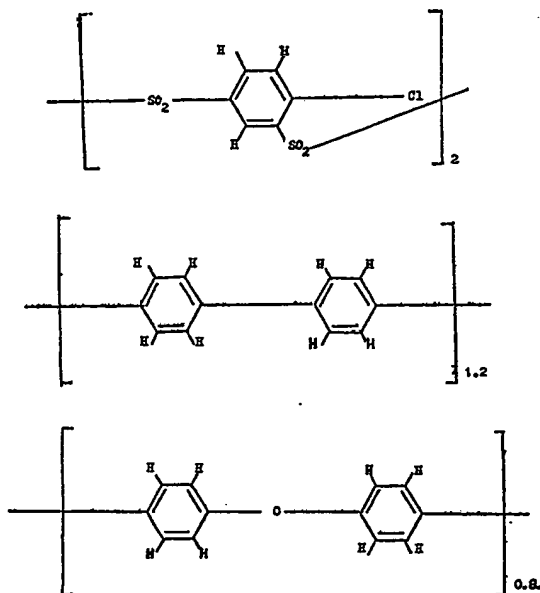
d) polymers consisting of repeating units of the following formulae in the numerical proportions shown:



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e) polymers consisting of repeating units of the following formulae in the numerical proportions shown:



In no case is more than one simple $-\text{O}-$ linking group attached to the same phenyl group in a polymer. This of course does not apply to the case where an oxygen atom linking two phenyl groups forms part of a ring linking two phenyl groups in an aromatic group A such as the dibenzofuran group.

The polymers according to the invention are strong and form tough, flexible, orientable films and filaments of excellent physical properties. Also they have low weight loss when heated in air to high temperature.

They can be extruded, drawn, oriented or otherwise formed into articles by conventional methods used to shape thermoplastic resins, without serious degradation; and the articles thus produced have a high degree of strength, toughness, flexibility and good appearance. They have excellent dielectric properties and retain these properties at high temperatures. By heating at a temperature below the melting point (i.e. annealing), or by orienting, crystallinity can be developed in a number of the polymers.

The polymers of the invention are thermoplastic and soften at relatively high temperatures. They melt at temperatures ranging from the order of 200°C to above 400°C . They are extremely stable, and can withstand temperatures of 400°C or even higher without serious degradation.

The polymers of the invention are soluble in concentration of 10 percent in phenol at 175°C which indicates their substantially

linear, non-crosslinked nature. They are also soluble in concentrated sulphuric acid and in N-methyl pyrrolidinone, producing stable solutions.

Additionally, many of the new polymers are soluble in such solvents as N,N-dimethyl formamide, dimethyl sulphoxide and pyridine. Some of them also being soluble in halogenated solvents such for example as methylene chloride. The solutions which result are in some instances useful for casting of films and spinning of fibres.

The stability of the polymers includes resistance to hydrolytic and oxidizing media. Thus, for example, the polymers may be recovered unchanged from their solution in concentrated sulphuric acid merely by dilution with water. Likewise, they can be heated under pressure in the presence of aqueous acids or bases without hydrolysis.

The toughness of thermoplastic materials is known to be an index of their utility for use as films or moulded items. Toughness as a property can be measured by subjecting a film of polymer from 3 to 7 mils thick to repeated creasing by folding a strip of the film double and creasing, followed by refolding the film back upon itself on the same line and again creasing, as one cycle. The number of creasing cycles withstood by the film before breaking at the crease line is referred to as the "degree of toughness". Failure to withstand the initial creasing rates a degree of toughness of zero; if the film

breaks on the second cycle, the degree of toughness is one, and so on.

The heat resistance of a polymer can be determined by thermogravimetric analysis (often abbreviated to TGA), i.e., measuring the loss of weight of the polymer while heating to high temperature. For example, a useful test is provided by simultaneously heating up and weighing a 100mg. sample of the polymer in an oven, in air, from ambient temperature to about 400°C—500°C, at the rate of 7°C. temperature increase per minute, to determine any weight loss. A weight loss of 5 percent or less in this test shows excellent stability of the polymer at the highest temperature used.

The polymers of the invention have various uses in numerous areas of application. They can be used to make films and fibres or moulded articles in any desired shape, either alone or mixed with for example fillers or glass fibres. They are usefully laminated with glass fibres or glass cloth. They can also be used as adhesives or coatings, to impregnate the surface of various materials or to form a surface film thereon. They are useful for example as wire coatings, tubes, pipes and sheets.

The polymers are particularly useful in applications where their high dielectric properties are of importance, as in electrical insulating materials, and particularly where severe and corrosive ambient conditions are found.

The invention comprehends a process for the production of polyarylsulphones which comprises heating, in the presence of a catalytic amount of an anhydrous Lewis acid, a mixture of a compound of the formula:



and a compound of the formula:



in which R represents a y-valent aryl group, R' represents a w-valent aryl group, X represents bromine or chlorine, and y is 2 when

w is 0 and y is 1 when w is 1, the compound of the formulae



and

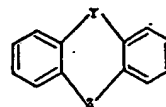


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and their relative proportions being chosen so that in the polyarylsulphone produced from 10 to 50 percent of the units L represent the simple linkage —O—.

Preferred arylsulphonyl halides for use in the process are the sulphonyl chlorides.

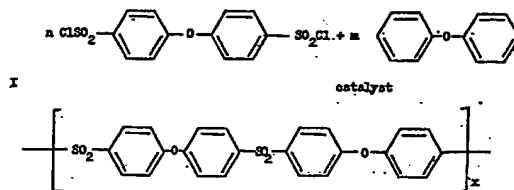
The aryl moieties R and R' of the foregoing formulae each contain at least two aromatic rings which may be substituted but which are free from hetero nitrogen atoms. Such aryl moieties useful in the process of the invention include for example biphenyl, naphthalene, anthracene, diphenylmethane, diphenyl ether and diphenyl sulphide; as well as those of the formula:



in which Y represents —O—, —S— or a carbon-carbon valence bond and Z represents —O—, —S— or —CH₂—. Moieties exemplified by the latter formula include for example xanthene, dibenzodioxin, fluorene, dibenzofuran, thianthrene, dibenzothiophene, dibenzo-1,4-thioxane and thiazathene.

In one embodiment, the process in accordance with the invention consists in the condensation of certain difunctional monomers in which y is 2, thus containing two sulphonyl halide groups, together with aromatic compounds in which w is zero, in the presence of Lewis acid catalysts. In carrying out the reaction, the halogen on each of the aromatic sulphonyl halide groupings reacts with a hydrogen atom of the aromatic compound.

The reaction is more specifically illustrated by the following series of equations:



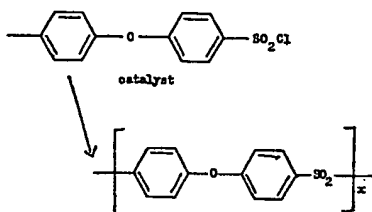
It will be apparent that as n and m must be the same in this specific illustration of the reaction, the resulting polymer will contain

approximately 50 percent —O— groups. In the formula x is a number which is an average of the number of repeating units present in

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the polymer chains, which, of course, varies depending upon the conditions of polymerisation.

- Another aspect of the condensation process of the invention employing monomers which are self-condensable, is illustrated by the following reaction:



In this case, y is 1 and w is 1.

- In this specific instance, polymers containing approximately 50 percent of —O— linking groups will be obtained.

- If a mixture of biphenyl sulphonyl chloride and diphenyl ether sulphonyl chloride is used, polymers having varying ratios of —O— and $\text{—SO}_2\text{—}$ linking groups will be formed. When 10 mole percent of the diphenyl ether sulphonyl chloride and 90 mole percent of biphenyl sulphonyl chloride are used, approximately 10 percent of the linking groups are —O— .

- Comonomers useful in reaction of type I, to produce homo- and copolymers, are exemplified by p,p'-diphenyl ether disulphonyl chloride, p,p'-biphenyl disulphonyl chloride, 2,7-fluorene disulphonyl chloride, 2,8-dibenzofuran disulphonyl chloride, 2,7-naphthalene disulphonyl chloride, p,p'-diphenyl sulphide disulphonyl chloride, diphenyl ether, dibenzofuran, fluorene, diphenylene dioxide and naphthalene. Monomers of the type useful in the process as illustrated by reaction II are exemplified by p-diphenyl ether monosulphonyl chloride and naphthylphenylether monosulphonyl chloride. Comonomers such for example as p-biphenyl monosulphonyl chloride, 2-fluorene sulphonyl chloride, 2-dibenzofuran sulphonyl chloride and 2-naphthalene sulphonyl chloride and 2-naphthalene sulphonyl chloride can be added to such monomers as p-diphenyl ether monosulphonyl chloride to change the ratio of —O— linking groups in the finished polymer.

- The individual aromatic nuclei in the monomers useful in the process of the invention are carbocyclic, e.g. benzene or naphthalene, and, as described above, they may be bonded together directly, or through an ether linkage, a methylene group or other small linking group, or a condensed ring system. Mixtures of monomers can be employed to form copolymers.

The underlying principle for the wide choice of operable monomers for the process appears to be the deactivating effect of the sulphonyl group on the aromatic ring to which it is or becomes attached. This deactivation is sufficient to prevent any significant amount of higher than monosulphone formation in any one ring. Branching and crosslinking are thus suppressed.

Any of the above monomers or comonomers can be further substituted with small non-reactive substituents on the aromatic nuclei. Thus, the aromatic nuclei may additionally bear alkyl or perfluoroalkyl groups, for example methyl, ethyl, propyl and hexyl groups; lower alkoxy groups, for example methoxy, ethoxy and butoxy groups; halogen atoms, for example chlorine or bromine, or other similar small substituents which are inert under the conditions of the poly condensation reaction.

The processes of this invention, broadly speaking, are carried out utilizing either melt condensation or solution condensation procedures, involving the repeated reaction between an aromatic sulphonylchloride group and an aromatic hydrogen atom by heating to a temperature of from 100 to 250°C. in the presence of a condensation catalyst.

It is generally preferred to utilize an inert solvent in carrying out the polymerisation process in order to increase the fluidity of the reaction mixture. The preferred solvents are chlorinated aliphatic and aromatic hydrocarbons, for example, s-tetrachloroethane, methylene chloride, and Aroclor (Registered Trade Mark) which is highly chlorinated biphenyl and diphenyl ether, or aliphatic and aromatic sulphones, for example, dimethyl sulphone, tetramethylene sulphone and p,p'-dichlorodiphenylsulphone, or aliphatic and aromatic nitro compounds, for example, 1-nitropropane, nitrobenzene, and 3,4'-dichloronitrobenzene.

Effective condensation catalysts are anhydrous Lewis acids, also known as Friedel-Crafts catalysts, for example ferric chloride, aluminium chloride, zinc chloride and the chlorides of antimony. Anhydrous hydrofluoric acid, or trifluoromethane sulphonic acid also may be used as catalysts.

The particularly preferred catalysts are salts and oxides of iron, e.g. ferric chloride, ferric bromide, ferric fluoride and ferric oxide. Ferrous chloride, ferric sulphate and ferrous-ferric oxide also can be effectively utilized as catalysts because these compounds are converted into ferric chloride by reaction with the sulphonylchloride monomer under the conditions of the polymerisation. These are generally found to be effective in amount of from 0.05 to 0.5 mole percent, based on the amount of monomer present. Greater proportions of catalyst may be utilized but this is generally unnecessary and is ordinarily avoided,

because larger amounts can adversely effect the degree of polymerisation and the separation of the catalyst from the polymer may prove difficult.

- 5 To effect the polycondensation the monomers or comonomers are generally first heated in the presence of an inert solvent to a temperature sufficient to obtain a uniform melt. Commonly this is achieved at a temperature ranging from 100 to 200°C., although temperatures of from 25 to 250°C. may be used. After a uniform melt is obtained the condensation catalyst is added and the mixture is maintained at a temperature of from 100 to 250°C. for from one hour to twenty hours, to complete the polymerisation. High molecular weight polyaryl sulphones are produced in good yields in this manner as is shown by the examples which follow.

- 20 The following Examples are given by way of illustration of the invention. In the Examples all parts are by weight, unless otherwise specified. Inherent viscosities of the polymers are determined in accordance with the following equation:

$$\eta_{\text{in}} = \frac{\ln \eta_{\text{rel}}}{C}$$

- 30 The relative viscosity (η_{rel}) is determined by dividing the flow time in a capillary viscometer of a dilute solution of the polymer by the flow time for the pure solvent. The concentration (C) is 1.0 gram of polymer per 100 ml. of solution and the measurements are made at a temperature of 25°C. in dimethyl formamide solution, unless otherwise noted.

EXAMPLE 1.

A mixture of 37.0 g. of diphenyl ether disulphonylchloride, 17.0 g. of diphenyl ether and 40 g. of dimethyl sulphone was placed in a 250 ml. flask fitted with a mechanical stirrer and a gas outlet. The flask was heated in an oil bath to 120°C. The reaction mixture was slowly stirred after a uniform melt had been obtained and 60 mg. of sublimed ferric chloride were added to initiate the polycondensation reaction. The liberated hydrogen chloride gas was discharged to a water trap. To complete the polymerisation the reaction mixture was heated at 120°C. for 5 hours, then at 140°C. for 15 hours and finally at 170°C. for 5 hours. The thick viscous mass obtained was dissolved in 450 ml. of hot dimethylformamide and the polymer was recovered by pouring the solution into 1.5 l. of methanol. The precipitated poly(diphenyl ether) sulphone was recovered by filtration, washed with hot water and dried at 120°C. under reduced pressure. The yield was 45 g. The polymer had a melting range of 260—280°C.; an inherent viscosity of 0.45 and was soluble in dimethylformamide, dimethyl sulfoxide, pyridine, and dichloromethane. The x-ray diffraction pattern revealed a completely amorphous structure for the polymer. This polymer had approximately 50% —O— linking groups in the polymer backbone.

A portion of the polymer was compression molded between sheets of aluminium foil at 580°F. The resulting film was transparent, flexible and tough. Clear, tough films were also prepared by casting the polymer from a 15—20% solution in dimethylformamide and evaporating the solvent at 50—100°C. Samples of such films displayed the following physical properties:

Density at 25°C.	1.371
Refractive Index	1.652
Tensile Strength (psi)	9,000
Modulus of Elasticity (psi)	150,000
Elongation (%)	10
Heat Penetration Temp. (°C.)	207
Flammability	Self extinguishing
Water Absorption (% at 25°C.)	2.1
Volatilization Temp. (°C. where 10% wt. loss occurs in the thermogravimetric analysis)	415

Electrical Properties	Temp. °C.	Frequency			
		100 c	1 kc	10 kc	100 kc
Dielectric Constant at	23	4.31	4.31	4.31	4.30
	75	4.10	4.06	4.04	4.02
	125	4.06	4.04	4.02	4.01
	175	4.09	3.99	3.99	3.99
	225	3.84	3.84	3.82	3.78
	275	5.40	4.56	4.23	4.05
Dissipation Factor in percent at	23	0.38	0.37	0.48	0.48
	75	0.23	0.26	0.32	0.38
	125	0.22	0.26	0.21	0.34
	175	0.35	0.20	0.31	0.38
	225	0.54	0.28	0.22	0.44
	275	28.37	12.69	5.98	3.19
Volume Resistivity at in ohm-cm.	23	1.7×10^{15}			
	75	7.9×10^{15}			
	125	1.1×10^{15}			
	175	1.3×10^{13}			
	225	3.0×10^{12}			
	275	2.2×10^{11}			

Corona stability at 500 v/mil., 40% humidity: 1000 hours

5 The foregoing electrical test values (low and flat value for the dissipation factor and dielectric constant up to high temperatures) indicate that the poly(diphenyl ether) sulphone has a high degree of utility in the field of electrical insulation.

EXAMPLE 2.

10 A mixture of 33.6 g. of p,p'-biphenyl disulphonylchloride, 17.0 g. of diphenyl ether and 36 g. of Arochlor 1248 (50% chlorinated biphenyl) was placed in a 250 ml. flask and heated to about 180°C. to obtain a uniform melt. The mixture was then allowed to cool to about 150°C. and after addition of 40 mg. of sublimed ferric chloride it was heated for 1 hour at temperatures gradually increasing to 200°C. The evolved hydrogen chloride was discharged to a water trap. To complete the polymerisation the flask was heated at 200°C. for 15 hours. The product was dissolved in 150 ml. of hot dimethylacetamide

and further diluted with dimethylacetamide to a volume of 500 ml. The polymer was recovered by pouring the hot solution into 2 l. of methanol and filtration of the precipitate. After washing with hot water and drying, 44 g. of poly(biphenyl-diphenyl ether) sulphone copolymer was obtained. The polymer showed a melting range of 310—330°C. and was soluble in dimethylformamide, dimethyl sulphoxide, and pyridine. X-ray diffraction studies revealed an amorphous structure for the polymer. The inherent viscosity was 0.40 and the polymer contained about 33 percent of —O— linking groups.

A portion of the polymer was compression molded to a film at 650°F. The resulting film was transparent, flexible and tough. Clear and flexible films were also prepared by casting the polymer from a 15—20% solution in dimethylformamide on a glass or metal plate. Samples of such films displayed the following physical properties:

Density at 25°C.	1.35
Refractive Index	1.65
Tensile Strength (psi)	5,800
Modulus of Elasticity (psi)	115,000
Elongation at break (%)	5—10
Heat Penetration (°C.)	250
Flammability	Self extinguishing
Water Absorption (% at 25°C.)	2.9
Volatilization Temp. (°C. where 10% wt. loss occurs in the thermogravimetric analysis)	440

Electrical Properties	Temp. °C.	Frequency			
		100 c	1 kc	10 kc	100 kc
Dielectric Constant at	22	3.51	3.50	3.48	3.47
	125	3.50	3.47	3.44	3.43
	225	3.03	3.59	3.57	3.55
	275	3.76	3.62	3.57	3.56
Dissipation Factor in percent at	22	0.31	0.24	0.30	0.51
	125	0.42	0.30	0.30	0.36
	225	1.38	0.52	0.40	0.38
	275	7.79	1.59	0.60	0.45
Volume Resistivity at in ohm-cm.	22	8.69×10^{16}			
	125	1.22×10^{16}			
	225	3.12×10^{12}			
	275	1.30×10^{11}			

EXAMPLE 3.

5 A mixture of 18.5 g. of 2,8-dibenzofuran disulphonylchloride, 8.5 g. of diphenyl ether and 20 g. of Arochlor 1248 was placed in a polymerisation tube of 200 ml. capacity and heated to about 190°C. to form a uniform melt. The mixture was then allowed to cool to about 150°C. After addition of 20 mg. of sublimed ferric chloride the reaction temperature was increased within 2 hours to 215°C. and then maintained at 215°C. for 20 hours by means of a methyl salicylate vapour bath. The solid reaction product thus obtained was dissolved in 250 ml. of hot dimethylacetamide and the solution poured into 1 l. of vigorously

stirred methanol. The precipitated poly(dibenzofurandiphenyl ether) sulphone copolymer was filtered off, washed with hot water and dried. The polymer showed a melting range of 320—350°C. and was soluble in dimethylformamide, dimethyl sulphoxide and pyridine. The inherent viscosity was 0.39. Thermogravimetric analysis indicated a weight loss by volatilization of 10% at 420°C.

Transparent, flexible films were obtained from the polymer by pressing at 680°F. or casting from a 20% solution in dimethylformamide. The following test values were obtained from electrical measurements on pressed films:

	Temp. °C.	Frequency			
		100 c	1 kc	10 kc	100 kc
Dielectric Constant at	23	4.09	4.07	4.05	4.00
	125	3.16	3.12	3.11	3.09
	225	3.51	3.49	3.48	3.47
	300	3.46	3.35	3.29	3.26
Dissipation Factor in percent at	23	0.49	0.43	0.53	0.98
	125	0.60	0.46	0.42	0.39
	225	0.69	0.49	0.41	0.33
	300	6.46	2.15	0.97	0.62
Volume Resistivity at in ohm-cm.	23	4.82×10^{15}			
	125	4.26×10^{14}			
	225	3.17×10^{13}			
	300	2.22×10^{11}			

EXAMPLE 4.

5 A charge of 16.5 g. of 2,7-naphthalene di-
sulphonylchloride, 8.5 g. of diphenyl ether
and 20 g. of Arochlor 1248 was placed in
a 200 ml. polymerisation tube and heated to
about 150°C. to form a uniform melt. After
addition of 20 mg. of sublimed ferric chloride
10 the temperature was increased within 2 hours
to about 200°C. and then maintained at
196°C. for 20 hours by means of an ethylene
glycol vapour bath. The product was dissolved
in 250 ml. of hot dimethylformamide and the
15 solution was poured into 1 l. of stirred
methanol. The resulting precipitated poly-

(naphthalenediphenyl ether) sulphone copoly-
mer was filtered off, washed with hot water
and dried. The polymer showed a melting
range of 290—320°C. and was soluble in
dimethyl formamide and dimethyl sulphoxide. 20
The inherent viscosity of a 1% solution is
conc. sulphuric acid was 0.36. Thermogravi-
metric analysis indicated a weight loss due
to volatilization of 10% at 425°C.

Self-supporting transparent films were pre- 25
pared from the polymer by pressing at 650°F.
Electrical measurements made on the films
showed the following values:

	Temp. °C.	Frequency			
		100 c	1 kc	10 kc	100 kc
Dielectric Constant at	23	3.88	3.86	3.84	3.80
	125	3.19	3.16	3.13	3.21
	175	3.10	3.07	3.01	3.00
	225	3.78	3.71	3.70	3.62
	250	3.84	3.77	3.71	3.66
Dissipation Factor in percent at	23	0.51	0.39	0.52	0.96
	125	0.92	0.85	0.52	0.48
	175	1.38	0.87	0.69	0.56
	250	3.57	1.40	0.94	0.82
Volume Resistivity at in ohm-cm.	23	2.22×10^{15}			
	125	1.18×10^{14}			
	175	1.55×10^{13}			
	225	2.86×10^{12}			
	250	6.21×10^{11}			

EXAMPLE 5.

A charge of 36.7 g. of p,p'-diphenyl ether disulphonylchloride and 16.9 g. of diphenylmethane was placed in a 250 ml. flask and heated to 160°C. After addition of 20 mg. of sublimed ferric chloride, the flask was connected to a trap cooled by liquid nitrogen and heating was continued at 160°C. After 30 minutes the flask was cautiously evacuated to 1 mm. Hg pressure and heated for another 30 minutes at temperatures rising from 160 to 200°C. After cooling, the solid foam filling the flask was broken up and pulverized. The product was then reheated under 1 mm. Hg pressure for 2 hours at temperatures rising from 200 to 240°C. The reaction product was dissolved in 450 ml. of hot dimethylform-

amide and the solution was poured into 1.5 l. of stirred methanol. The precipitated poly-(diphenyl ether-diphenyl methane) sulphone copolymer thus obtained was removed by filtering, washed with hot water and dried. The polymer showed a melting range of 230—250°C. and was soluble in dimethylformamide, dimethyl sulphoxide, pyridine and dichloromethane. The inherent viscosity was 0.34.

Self-supporting, transparent and flexible films were prepared from the polymer by pressing at 550°C., or by casting from a 20% solution in dimethylformamide and evaporating the solvent at 50—100°C. The following values were obtained from electrical measurements on such films:

	Temp. °C.	Frequency			
		100 c	1 kc	10 kc	100 kc
Dielectric Constant at	23	3.92	3.90	3.88	3.85
	75	3.87	3.83	3.80	3.77
	125	3.88	3.84	3.80	3.78
	175	3.91	3.87	3.83	3.80
	200	3.99	3.94	3.89	3.88
Dissipation Factor in present at	23	0.48	0.40	0.44	0.64
	75	0.61	0.57	0.55	0.55
	125	0.65	0.62	0.63	0.58
	175	0.91	0.67	0.67	0.87
	200	1.79	0.86	0.70	0.77
Volume Resistivity at in ohm-cm	23	1.88 × 10 ¹⁶			
	75	3.99 × 10 ¹⁵			
	125	1.15 × 10 ¹⁴			
	175	3.05 × 10 ¹³			
	200	1.43 × 10 ¹³			

EXAMPLE 6.

A mixture of 54 g. of p-diphenyl ether monosulphonylchloride and 30 g. of dimethylsulphone was placed in a 250 ml. flask fitted with a mechanical stirrer and a gas outlet. The flask was heated to 120°C. and after a uniform melt was obtained, 40 mg. of sublimed ferric chloride were added while the reaction mixture was slowly stirred. The evolved hydrogen chloride gas was discharged into a water trap. After 3 hours heating at temperatures rising from 120 to 160°C. the stirring was discontinued. During an additional 3 hours of heating the temperature was gradually increased to 190°C. to complete the polymerisation. The solid product obtained after cooling to room temperature was recovered by breaking the flask and then was finely ground in a mill. The ground material was heated for 3 hours in 500 ml. of boiling water to extract and remove the dimethyl-

sulphone solvent. The water-insoluble poly-(diphenyl ether) sulphone was filtered off, washed with fresh water and dried. The polymer showed a melting range of 260—280°C. and was soluble in dimethylformamide, dimethylsulphoxide, pyridine and dichloromethane. The inherent viscosity of a 1% solution in bromochloromethane was 0.47.

A portion of the polymer was pressed at 570°F. into transparent, flexible and tough films. A colourless, clear film was also obtained from casting a 20% solution of the polymer in dichloromethane on a glass plate and evaporating the solvent at room temperature. The film was lifted from the plate and further dried under reduced pressure at temperatures gradually rising from 20 to 100°C. within 8 hours. Samples of a film of poly-(diphenyl ether) sulphone thus prepared displayed the following properties:

	Temp. °F.	
Tensile strength (psi)	73	10,300
	100	8,100
	200	7,500
	300	5,200
	400	2,900
	450	300
	500	40*
*after repull at room temperature, 12,800 psi		
Modulus of elasticity (psi) at	73	246,000
	100	240,000
	200	150,000
	300	125,000
	400	94,000
	450	4,000
	500	—**
**after repull at room temperature, 320,000 psi.		
Elongation at break (%) at	73	13
	100	5
	200	5
	300	5
	400	5
	450	approx. 160
	500	approx. 500***
***after repull at room temperature, 50%.		

EXAMPLE 7.

A mixture of 30 g. (0.112 mole) of p-di-phenyl ether sulphonylchloride, 20 g. (0.080 mole) of p-biphenyl sulphonylchloride and 35 g. of dimethylsulphone was placed in a 250 ml. flask fitted with a mechanical stirrer and a gas outlet. The flask was heated to about 130°C. and after a uniform melt had formed 40 mg. of sublimed ferric chloride were added while the reaction mixture was stirred slowly. Heating and stirring were continued for 15 hours temperatures gradually rising from 130 to 160°C. and finally for 6 hours at 160°C. to 190°C. The hydrogen chloride gas evolved during the polymerisation was eliminated by a slow stream of nitrogen leading to a water trap. The highly viscous mass thus obtained was diluted with 200 ml. of N,N-dimethylacetamide and poured in a thin stream into warm water containing a small amount of hydrochloric acid. The precipitated poly-(diphenyl ether-biphenyl) sulphone copolymer containing 37% oxygen linkages was ground up in a high speed blender, extracted twice for several hours with boiling distilled water and dried. The polymer showed a melting range of 300—320°C. and was soluble in dimethyl formamide, dimethyl sulphoxide, pyridine and bromochloromethane. The inherent viscosity was 0.50.

Transparent and flexible films were prepared from a portion of the polymer by pressing between sheets of aluminium foil at 620°F. and subsequently quenching in cold water. Samples of these films showed tensile strength of 10,000 psi, modulus of elasticity of 90,000 psi and elongation at break of 20%.

The aromatic sulphonyl halide starting compounds are readily prepared by methods known to the art. Thus, for example, the selected aromatic compound, in solution in an inert solvent such as for example chloroform, is first reacted with an equimolar amount of chlorosulphonic acid. The mixture is subsequently treated with an excess of thionyl chloride containing about 10% dimethylformamide, and heated to refluxing for several hours. After removal of the excess thionyl chloride and solvent by distillation, the reaction mixture is washed with water. The product is purified by distillation or recrystallisation.

EXAMPLE 8.

A charge of 100 g. of 2-dibenzofuran sulphonylchloride and 60 g. dimethylsulphone was placed in a 500 ml. flask and heated to about 140°C. until a uniform melt had been formed. Sublimed ferric chloride (80 mg.) was then added and heating was continued for 15

hours at temperatures gradually rising to 180°C. and for an additional 6 hours at 210–225°C. The evolved hydrogen chloride gas was then discharged to a water trap. The solid reaction product was ground up, dissolved in 700 ml. of hot N-methylpyrrolidone and precipitated in water. The precipitated poly(dibenzofuran sulphone) was recovered by filtration, washed twice with boiling water containing a small amount of hydrochloric acid and dried. The polymer showed a melting range of 410–440°C. The inherent viscosity of a 1% concentrated solution in a mixture of 60 g. phenol and 40 g. s-tetrachloroethane was 0.45. The x-ray diffraction pattern indicated a crystalline structure for the polymer.

EXAMPLE 9.

Dibenzodioxin monosulphonylchloride was prepared from dibenzodioxin with equimolar amounts of chlorosulphonic acid in chloroform medium and subsequent treatment at reflux temperature with excess thionylchloride containing 10% dimethylformamide. The dibenzodioxin monosulphonylchloride was purified by recrystallization from carbon tetrachloride and had a melting point of 92–93°C.

The polymer was prepared as follows:

Dibenzodioxin monosulphonyl chloride (50 g.) and dimethylsulphone (35 g.) were placed in a 250 ml. flask and heated to 130°C. to form a uniform melt. Then 50 mg. sublimed ferric chloride were added and the mixture was heated for 15 hours at temperatures rising from 130 to 160°C. and then for 5 hours at 200–210°C. The hydrogen chloride gas evolved during the polymerisation was eliminated by a slow stream of nitrogen leading to a water trap. The solid reaction product was ground up and dissolved in 500 ml. of boiling phenol. The solution was filtered and poured into 2 l. of dimethylformamide. The poly(dibenzodioxin sulphone) separated as a crystalline precipitate. It was filtered, washed carefully with acetone and hot water and dried. The polymer showed a melting range of 350–370°C. and an inherent viscosity of 0.20 as a 1% concentrated solution in a mixture of 60 g. phenol and 40 g. s-tetrachloroethane.

EXAMPLE 10.

When fluorene, xanthene, dibenzo 1,4-thioxane, dibenzo 1,4-dithiane, and thioxanthene, respectively, were converted to the respective monosulphonyl chlorides, and each was polymerised by the process of Example 9, these were obtained: poly(fluorene sulphone), poly(xanthene sulphone), poly-dibenzo 1,4-thioxane sulphone, poly(dibenzo 1,4-dithiane sulphone) and poly(thioxanthene sulphone).

The use of a mixture of equimolar amounts of the monosulphonyl chloride derivation of

two aromatic compounds of this group produces a copolymer. Thus using a mixture of 100 g of fluorene monosulphonyl chloride, about 100 g of 2-dibenzofuran monosulphonyl chloride and about 100 mg of ferric chloride yields a copolymer with randomly interspersed fluorene sulphone and dibenzo furane sulphone groups in the polymer chain.

EXAMPLE 11.

A mixture of 50 g of 2-naphthalene sulphonylchloride and 30 g of dimethylsulphone was heated to 150°C. to form a uniform melt. Then 50 mg. of sublimed ferric chloride were added and the heating was continued for 5 hours at temperatures rising from 150 to 190°C. and for 15 hours at 200°C. The product was allowed to cool, ground into a fine powder, extracted twice (for several hours with boiling water to remove the dimethyl sulphone solvent) and dried. The poly-(naphthalene sulphone) thus obtained showed a melting range of 290–310°C. and an inherent viscosity of 0.18 in a 1% concentrated solution in a mixture of 60 g. phenol and 40 g. s-tetrachloroethane. The polymer was practically colourless and was soluble in dimethyl sulphoxide, N-methyl pyrrolidone and phenol.

EXAMPLE 12.

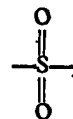
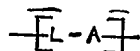
A mixture of 16.6 g. of 2,7-naphthalene disulphonyl chloride, 7.7 g. of biphenyl and 18 g. of Arochlor 1248 (50% chlorinated biphenyl) was heated in a flask to 160°C. After a uniform melt had formed, 30 mg. of sublimed ferric chloride were added and heating was continued for 3 hours at temperatures rising from 160 to 220°C. The product was allowed to cool, ground up and dissolved in 200 g. of hot phenol. The solution was poured into a mixture of 2 parts of dimethyl formamide and 1 part of methanol. The poly-(naphthalenebiphenyl) sulphone copolymer separated as a crystalline precipitate. It was recovered by filtration, washed carefully with methanol and hot water containing a small amount of hydrochloric acid and dried. The polymer showed a melting range of 330–350°C. and an inherent viscosity of 0.20 as a 1% concentrated solution in a mixture of 60 g. of phenol and 40 g. of s-tetrachloroethane. The polymer was colourless to somewhat yellow and was soluble in dimethylsulphoxide, phenol and N-methyl pyrrolidone.

Copolymers made by the above process, but using mixtures of biphenylsulphonylchloride and 2-naphthalene sulphonylchloride produce copolymers with varying numbers of naphthyl and biphenyl groups in the chain.

WHAT WE CLAIM IS:—

1. A thermoplastic, substantially linear soluble polymer which is capable of forming

self-supporting films, and which consists essentially of repeating units of the formula:



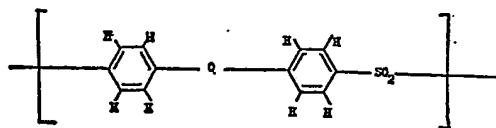
each aromatic group represented by A 10
being connected to no more than one
linkage L represented by the simple
linkage $-\text{O}-$,

5 in which A represents an aromatic group,
and in from 10 to 50 percent of the
units L represents the simple linkage
 $-\text{O}-$, and in the other units L repre-
sents the linkage

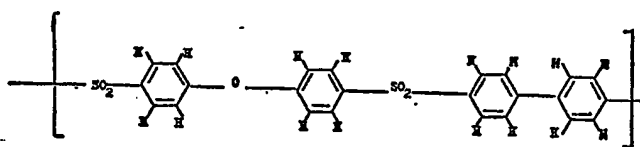
the polymer having an inherent viscosity (as
herein defined) of not less than 0.3, with 15
the exception of the following polymers a to e
when prepared by melt condensation:

a) polymers consisting of repeating units
being the formula:

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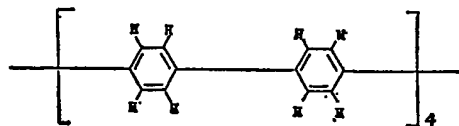
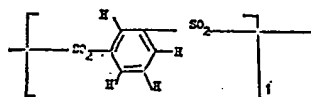
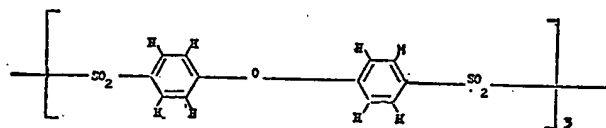


b) polymers consisting of repeating unit of the formula:

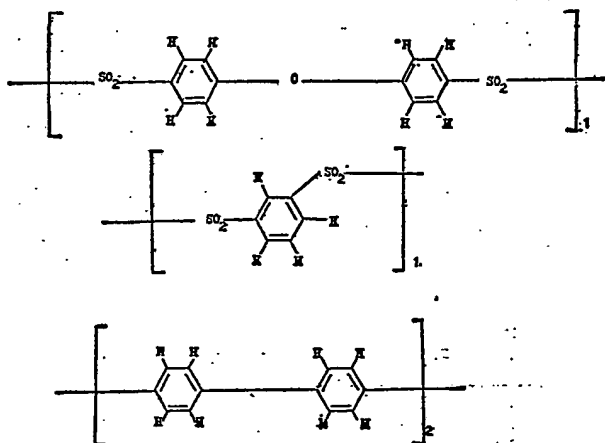


c) polymers of repeating units of the following formulae in the numerical proportions
shown:

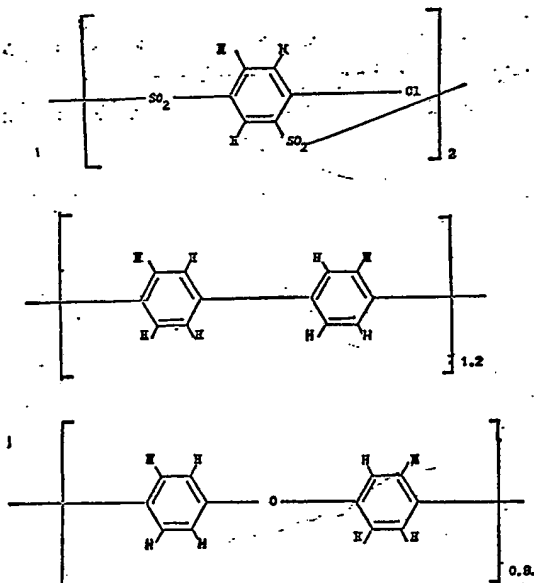
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d) polymers consisting of repeating units of the following formulae in the numerical proportions shown:

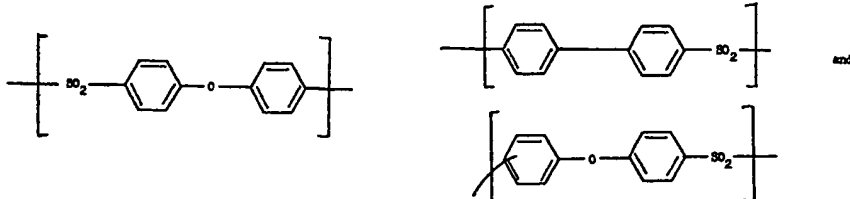


e) polymers consisting of repeating units of the following formulae in the numerical proportions shown:



2. A polymer as claimed in Claim 1 in which the aromatic group is a phenylene radical.

3. A polymer as claimed in Claim 1 containing repeating units of the formula:

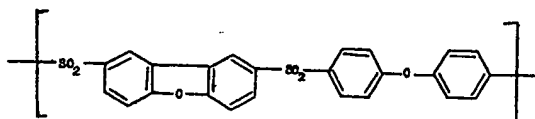


which has been prepared by solution condensation.

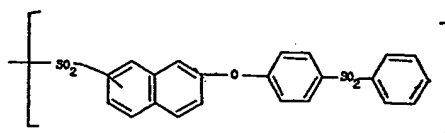
4. A polymer as claimed in Claim 1 containing repeating units of the formulae:

with the exception of the polymer prepared by melt condensation where the proportion of one repeating unit to the other 1:1.

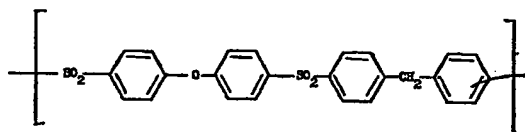
5. A polymer as claimed in Claim 1 containing repeating units of the formula:



6. A polymer as claimed in Claim 1 containing repeating units of the formula:



7. A polymer as claimed in Claim 1 containing repeating units of the formula:

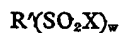


8. A thermoplastic, substantially linear soluble polymer substantially as herein described with reference to the Examples.

9. A process for the production of a polymer as claimed in any preceding claim which comprises heating a compound of the formula

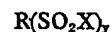


with a compound of the formula



in which R represents a y-valent aryl group, R' represents a w-valent aryl group, both groups R and R' each containing at least two aromatic rings, X represents bromine or chlorine and y is 2 when w is 0 and y is 1 when w is 1, in the presence of an anhydrous

Lewis acid catalyst, the compounds of the formulae



and



and their relative proportions being chosen so that in the polymer produced from 10 to 50 percent of the units L represent the simple linkage —O—.

10. A process as claimed in Claim 9 which is effected in the presence of a solvent.

11. A process according to Claim 9 and substantially as herein described with reference to the Examples.

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